

A Theoretical Study on the Gas- and Aqueous-Phase Photodegradation and Thermal Decomposition Channels of Pyruvic Acid

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Pyruvic acid (PA) is a key intermediate in the keto-acid chemistry of atmospheric aerosols. Currently, there is still a lack of fundamental understanding of the PA degradation processes in both gas and aqueous phase. In this work, several pathways leading to vinyl alcohol, acetaldehyde, and acetic acid were explored. These were determined by density functional theory (DFT) using B3LYP and coupled cluster method with singles and doubles correction using the second-order Møller–Plesset perturbation theory structures. The solvation model based on density (SMD) was used for the aqueous phase calculations. The Dunning-style cc-pVTZ basis set was used for all calculations. The most accessible thermal decomposition pathway is through the hydroxymethylcarbene (CH_3COH) intermediate, with an overall barrier height of 42.19 and 45.92 kcal/mol for gas and aqueous phase, respectively. All the pathways favor decomposition in solvation except for the acetaldehyde pathways. Moreover, using the time-dependent DFT, only the CH_3COH channel allows photodegradation to proceed within the 300-380 nm through the first triplet and singlet excited states.